TARGETING SINGLE COAL MACERALS WITH DENSITY GRADIENT CENTRIFUGATION EXPERIMENTS

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INTRODUCTION

Since density gradient centrifugation (DGC) techniques were introduced into coal science a little over ten years ago, continuous work has been done to separate and characterize coal macerals [1-11]. To date, good separations of the liptinite, vitrinite, and inertinite maceral groups have been reported, as have separations of individual maceral types including, sporinite, resinite, cutinite, vitrinite, pseudovitrinite, semifusinite and fusinite from coal and of alginite, sporinite, and amorphous kerogen from petroleum source rocks. Most of the separations have been verified both petrographically and chemically. Chemical analysis including chromatography and spectroscopy of these separated materials show them to have diverse bulk chemistry and chemical structures. Most recently, reactivity and combustion studies on separations of both maceral groups and single macerals have shown significant differences between them. The results of all of these studies have shown the extreme heterogeneity of coal and has improved our ability to predict the behavior of coal in any process of interest.

TARGETING SINGLE MACERALS

To obtain separations of single coal macerals from a particular coal, coal maceral groups (liptinite, vitrinite, and inertinite) must first be concentrated. The common procedure is to do an initial two gram DGC run to obtain a density profile. Two grams is the maximum sample capacity of the standard two liter centrifuge bowl and usually provides enough material to give a useful density profile, if the macerals are well liberated. The normal procedure is to reduce the coal sample to micrometer size to get reasonable liberation and a minimum of mixed phase particles. From the density profile, two density cut-points are chosen, one at the liptinite/vitrinite boundary and one at the vitrinite/inertinite boundary as illustrated in Figure 1. While these cut-points can be determined by inspection, a superior technique is to do the determination by petrographic methods including white light and fluorescence analysis. Any cut-point determinations not verified by petrography are immediately open to question. Once the cut-points are in hand, quantities of the various maceral groups are concentrated by centrifugation at the chosen densities serially. It should be noted that for some research, the separations of these maceral groups are sufficient and further subdivision is not required. However, the results of such research must indicate that maceral groups and not single macerals were used.

When the separation of single coal macerals is desired, two gram quantities of the maceral group concentrates are again processed in a DGC run over the appropriate but limited density range, e.g. 1.00 g/mL to the liptinite/vitrinite cut-point for the liptinite maceral group. Such density profiles of the maceral groups usually reveal structure that indicates the presence of a number of single macerals such as cutinite, resinite, and sporinite in the liptinite group.

SPECIAL TECHNIQUES FOR SEPARATING SINGLE MACERALS

There are a number of techniques that facilitate the separation of single macerals from coal. The three most useful are cryogenic treatment, demineralization, and semicontinuous centrifugation. While the usual techniques of micronization using a fluid energy mill or a jet mill will reduce the particle size of a sample to the micrometer range, some multiphase particles often persist. These can be reduced by immersing the sample in liquid nitrogen to freeze it and then rapidly thawing it out at room temperature. With this treatment, the multiphase particles tend to fracture along maceral boundaries. This process can be repeated with or without regrinding to achieve maximum liberation of the macerals.

Demineralization with HCl to eliminate carbonates and HF to eliminate silicates will both increase the yield of a DGC separation and increase the purity of a given density fraction by reducing mixed maceral/mineral phases. However, mineral sulfides

especially pyrite and mineral oxides will not be removed by this acid treatment. If any significant amounts of these minerals are present, a preliminary sink/float separation at a density of about 1.7 g/mL has been found to improve the DGC separation. In cases where pyrite is extremely fine-grained and well dispersed, separation results can be unsatisfactory.

When the target macerals are not very abundant and more than milligram to gram quantities are needed, semicontinuous centrifugation can be used. This technique has been well described [12-13] and allows kilograms of sample to be processed per day. Because it operates at only a single density per run, sequential runs are necessary to concentrate a target maceral.

DISCRIMINATING SAMPLE SELECTION
The techniques described above will usually achieve successful separations on most coals, however, much higher yields and much shorter processing times are possible, if there are no constraints on the choice of the original sample, i.e. the target maceral is specified and not its source [14-16]. While most coals are composed of 50 to 90% vitrinite as shown in the density profile in Figure 1, some coals particularly the Permian Gondwana coals of the southern hemisphere are dominated by inertinite macerals. The density profile of such a coal from South Africa is as shown in Figure 2. It has an inertinite content of over 70% and is clearly an excellent choice for inertinite maceral separation. Other humic coals have higher than normal contents of specific macerals, such as the resinite rich coals from the western U.S. (see Figure 3). Sapropelic coals are dominated by sporinite (cannel coal), alginite (boghead coal) and bituminite, and thus make good candidates for the separation of these macerals. Although these coal types are not abundant, they are ubiquitous. The density profiles of a typical boghead coal along with two different cannel coals are given in Figures 4, 5, and 6 respectively. When appropriate whole coals cannot be found, selected layers in particular coal seams can sometimes be used. The layers, called lithotypes, are specific associations of macerals that can be quite different from the average composition of the whole coal seam. A common lithotype and the easiest to collect is fusain. It is composed of inertinite macerals, mainly semifusinite and fusinite. An example is shown in Figure 7. The two main peaks are natural concentrations of semifusinite (lower density) and fusinite (higher density). The vitrain lithotype is a natural concentration of vitrinite. It can be hand-picked with only moderate effort. As shown in Figure 8, it gives a density profile that shows only vitrinite. Figure 9 shows a monomaceralic boghead coal that shows only alginite.

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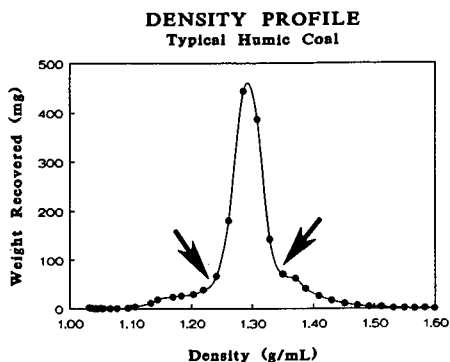
DENSITY PROFILE
Typical Humic Coal

Figure 1. A typical density profile of an humic coal. The main peak represents the vitrinite group macerals, the low density shoulder represents the liptinite group, and the high density shoulder represents the inertinite group. The arrows indicate typical cut-points between the macerals groups.
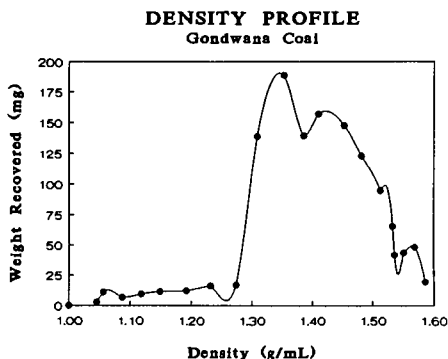
DENSITY PROFILE
Gondwana Coal

Figure 2. A typical density profile of an inertinite rich Gondwana coal. While the highest peak represents vitrinite the bulk of the sample is inertinite group macerals on the high density side of the vitrinite.

DENSITY PROFILE
Resinite Rich Coal
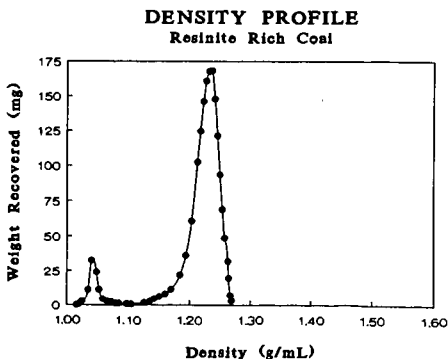
Figure 3. A density profile of a resinite rich coal from the western U.S. The major peak is the vitrinite maceral group, but the smaller very low density peak is resinite.
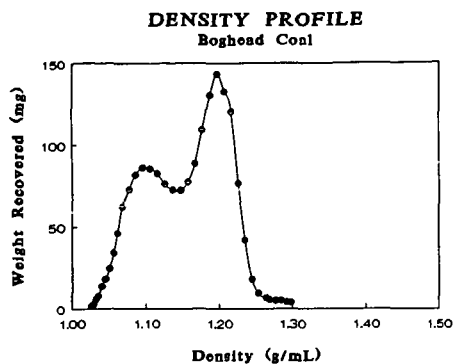
DENSITY PROFILE
Boghead Coal

Figure 4. A density profile of a boghead coal. The main peak represents the amorphous kerogen (bituminite?) matrix and the well defined low density peak is alginite.
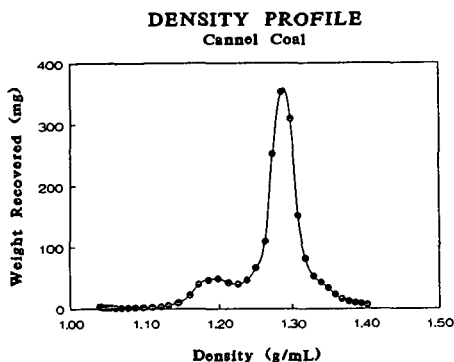
DENSITY PROFILE
Cannel Coal

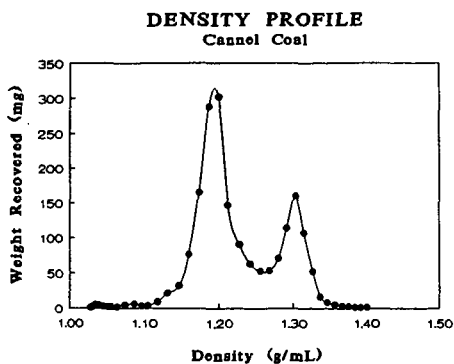Figure 5. A density profile of a cannel coal. The main peak is vitrinite and the low density peak is sporinite.

DENSITY PROFILE
Cannel Coal

Figure 6. A density profile of another cannel coal which is extremely sporinite rich. In this case the dominant peak is sporinite and the smaller peak is vitrinite.
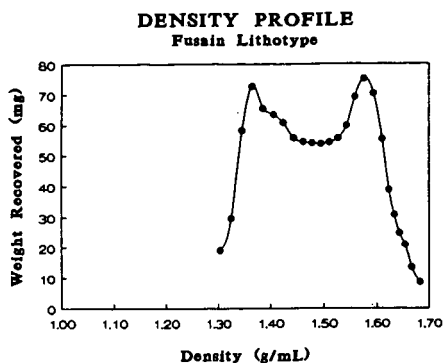
DENSITY PROFILE
Fusain Lithotype

Figure 7. A density profile of a fusain lithotype. Note that it contains only inertinite macerals. The two peaks represent semifusinite (lower density) and fusinite (higher density).
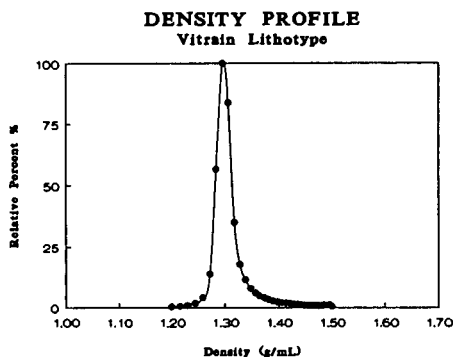
DENSITY PROFILE
Vitrain Lithotype

Figure 8. A density profile of a vitrain lithotype consisting of vitrinite and very little else.
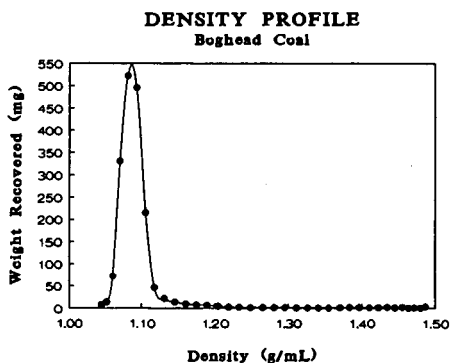
DENSITY PROFILE
Boghead Coal

Figure 9. A density profile of a boghead coal that is essentially momomaceralic consisting of alginite.